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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Flameproofed Thermoplastic Molding Materials

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Abstract of the Disclosure: Flameproofed, thermoplastic molding materials contain, as essential components,

- A) 10-98% by weight of a partly aromatic copolyamide, essentially composed of
  - a<sub>1</sub>) from 40 to 90% by weight of units derived from terephthalic acid and hexamethylenediamine,
  - a<sub>2</sub>) from 0 to 50% by weight of units derived from  $\epsilon$ -caprolactam and
  - a<sub>3</sub>) from 0 to 60% by weight of units derived from adipic acid and hexamethylenediamine,components a<sub>2</sub>) and/or a<sub>3</sub>) accounting in total for not less than 10% by weight of the total number of units,
- B) 1-30% by weight of a brominated polystyrene or a brominated styrene oligomer or of a mixture thereof,
- C) 1-15% by weight of a synergistic metal oxide or metal borate or a mixture thereof and in addition
- D) 0-60% by weight of a fibrous or particulate filler or a mixture thereof and
- E) 0-20% by weight of an elastomeric polymer.

Flameproofed thermoplastic molding materials

The present invention relates to flameproofed thermoplastic molding materials containing, as essential components,

- 5 A) 10-98% by weight of a partly aromatic copolyamide, essentially composed of
- 10 a<sub>1</sub>) from 40 to 90% by weight of units derived from terephthalic acid and hexamethylenediamine,
- a<sub>2</sub>) from 0 to 50% by weight of units derived from ε-caprolactam and
- 15 a<sub>3</sub>) from 0 to 60% by weight of units derived from adipic acid and hexamethylenediamine,
- components a<sub>2</sub>) and/or a<sub>3</sub>) accounting in total for not less than 10% by weight of the total number of units,
- 15 B) 1-30% by weight of a brominated polystyrene or a brominated styrene oligomer or of a mixture thereof,
- C) 1-15% by weight of a synergistic metal oxide or metal borate or a mixture thereof
- 20 and in addition
- D) 0-60% by weight of a fibrous or particulate filler or a mixture thereof
- and
- E) 0-20% by weight of an elastomeric polymer.

25 The present invention furthermore relates to the use of these molding materials for the production of moldings, and to the moldings obtainable using these molding materials as essential components.

30 Partially crystalline, partly aromatic copolyamides possess in particular high thermal stability, which is necessary for many applications. Because of the high melting point, flameproofing these polyamides presents problems since most conventional flameproofing agents have poor thermal stability and therefore cannot be incorporated without decomposition.

35 EP-A 299 444 discloses that nylon 66/6T and nylon 6/6T can be flameproofed with red phosphorus in the presence of stabilizers.

Molding materials of this type have the disadvantage that, owing to the intrinsic red color of the phosphorus and its pigment-like character, these molding materials cannot be given a paler color. In addition, the action of moisture and heat results in the formation of thermal oxidation products of phosphorus, such as phosphinic acids or oxyacids, which in turn present toxicological problems and on the other hand form conductive deposits. The reduced surface resistance greatly restrict the suitability of such moldings in the electrical sector.

DE-A 27 03 419 discloses polyamide molding materials which are flameproofed with brominated styrene oligomers and a synergistic metal oxide.

DE-A 15 70 395, DE-A 24 59 062 and DE-A 33 37 223 disclose the use of high molecular weight polystyrenes, brominated in the nucleus, as flameproofing agents for polyolefins, epoxy resins, styrene polymers, ABS and polyester molding materials.

Thermoplastic polyamides, especially those having a high melting point, such as nylon 6/6T, are usually processed at above 300°C. Particularly in the case of filler-reinforced polyamides, relatively high processing temperatures must be used. Furthermore, relatively high shear forces occur during incorporation of fillers, said shear forces resulting in further temperature increases, particularly local temperature peaks, for example on the glass fiber kneading block.

However, most of the known halogen-based flameproofing agents decompose at these temperatures, and corrosive gases may form and the moldings become discolored. Another disadvantage is that many halogen compounds, such as chlorinated or brominated aliphatic, cycloaliphatic or aromatic low molecular weight compounds, are highly toxic. Because of the poor compatibility of most low molecular weight halogen compounds with polyamides and their relatively high vapor pressure,

exudation of the flameproofing agents and hence the formation of deposits may occur.

5 It is an object of the present invention to provide flameproofed thermoplastic molding materials whose moldings have good electrical properties, in particular creep resistance and dielectric strength, and a good overall spectrum of mechanical properties. In addition, these moldings should have a pale intrinsic color and the flameproof properties and electrical properties should be  
10 very substantially independent of the type and amount of fillers.

We have found that this object is achieved, according to the invention, by the thermoplastic molding materials defined at the outset.

15 Preferred materials of this type and their use are described in the subclaims.

The novel thermoplastic molding materials contain, as component A), from 10 to 98, preferably from 35 to 97, in particular from 40 to 90, % by weight of a  
20 partly aromatic copolyamide having the composition described below.

The partly aromatic copolyamides A) contain, as component a<sub>1</sub>), from 40 to 90 % by weight of units derived from terephthalic acid and hexamethylenediamine. A small  
25 amount of the terephthalic acid, preferably not more than 10% by weight of the total amount of aromatic dicarboxylic acids used, may be replaced by isophthalic acid and other aromatic dicarboxylic acids, preferably those in which the carboxyl groups are in the para position.

30 In addition to the units derived from terephthalic acid and hexamethylenediamine, the partly aromatic copolyamides contain units derived from ε-caprolactam (a<sub>2</sub>) and/or units derived from adipic acid and hexamethylenediamine (a<sub>3</sub>).

35 The amount of units derived from ε-caprolactam is not more than 50, preferably from 20 to 50, in particular from 25 to 40, % by weight, while the amount of units

derived from adipic acid and hexamethylenediamine is not more than 60, preferably from 30 to 60, in particular from 35 to 55, % by weight.

5 The copolyamides may furthermore contain both units of  $\epsilon$ -caprolactam and units of adipic acid and hexamethylenediamine; in this case, it should be ensured that the amount of units which are free of aromatic groups is not less than 10, preferably not less than 20, % by weight. The ratio of units derived from  $\epsilon$ -caprolactam to those derived from adipic acid and hexamethylenediamine is not subject to any particular restriction.

10 Preferred copolyamides are those whose composition lies, in the ternary diagram, within the pentagon fixed by apices  $X_1$  to  $X_5$ , which are defined as follows:

15	$X_1$	40% by weight of units $a_1$ )
		60% by weight of units $a_3$ )
	$X_2$	60% by weight of units $a_1$ )
		40% by weight of units $a_3$ )
	$X_3$	80% by weight of units $a_1$ )
20		5% by weight of units $a_2$ )
		15% by weight of units $a_3$ )
	$X_4$	80% by weight of units $a_1$ )
		20% by weight of units $a_2$ )
	$X_5$	50% by weight of units $a_1$ )
25		50% by weight of units $a_2$ )

In the Figure, the pentagon fixed by these points is shown in a ternary diagram.

30 Polyamides containing from 50 to 80, in particular from 60 to 75, % by weight of units derived from terephthalic acid and hexamethylenediamine (units  $a_1$ )) and from 20 to 50, preferably from 25 to 40, % by weight of units derived from  $\epsilon$ -caprolactam (units  $a_2$ )) have proven particularly advantageous for many intended uses.

35 In addition to the units  $a_1$ ) to  $a_3$ ) described above, the novel partly aromatic copolyamides may furthermore contain minor amounts, preferably not more than 15, in particular not more than 10, % by weight of

further polyamide building blocks, as known from other polyamides. These building blocks may be derived from dicarboxylic acids of 4 to 16 carbon atoms and aliphatic or cycloaliphatic diamines of 4 to 16 carbon atoms and from aminocarboxylic acids or corresponding lactams of 7 to 12 carbon atoms. As suitable monomers of these types, suberic acid, azelaic acid, sebacic acid and isophthalic acid are mentioned here merely as typical dicarboxylic acids, 1,4-butanediamine, 1,5-pentanediamine, piperazine, 4,4'-diaminodicyclohexylmethane, 2,2-(4,4'-diaminodicyclohexyl)-propane and 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane as typical diamines, and capryllactam, enantholactam, omega-aminoundecanoic acid and lauro lactam as typical lactams and aminocarboxylic acids respectively.

The melting points of the partly aromatic copolyamides A) are from 260 to more than 300°C, this high melting point also being associated with a high glass transition temperature of, as a rule, more than 75°C, in particular more than 85°C.

Binary copolyamides based on terephthalic acid, hexamethylenediamine and ε-caprolactam contain about 70% by weight of units derived from terephthalic acid and hexamethylenediamine, melting points of about 300°C and a glass transition temperature of more than 110°C.

Binary copolyamides based on terephthalic acid, adipic acid and hexamethylenediamine (HMD) reach melting points of 300°C or more with lower contents of only about 55% by weight of units of terephthalic acid and hexamethylenediamine, the glass transition temperature not being quite so high as in the case of binary copolyamides which contain ε-caprolactam instead of adipic acid or adipic acid/HMD.

The partly aromatic copolyamides A) can be prepared, for example, by the process described in EP-A 129 195 and EP-A 129 196.

In this process, an aqueous solution of monomers,

ie. in this case the monomers which form the units  $a_1$  to  $a_3$ ), is heated to 250-300°C under superatmospheric pressure with simultaneous evaporation of water and formation of a prepolymer, the prepolymer and vapors are then continuously separated, the vapors are rectified and the entrained diamines are recycled. Finally, the prepolymer is passed into a polycondensation zone and is subjected to polycondensation under superatmospheric pressure of from 1 to 10 bar and at from 250 to 300°C. In this process, it is essential that the aqueous salt solution is heated under superatmospheric pressure of from 1 to 10 bar during a residence time of less than 60 seconds, the conversion advantageously being not less than 93% and the water content of the prepolymer not more than 7% by weight on emergence from the evaporator zone.

As a result of these short residence times, the formation of triamines is substantially prevented, so that the partly aromatic copolyamides A) generally have triamine contents of, preferably, less than 0.5, in particular less than 0.3, % by weight. High triamine contents can lead to a deterioration in the product quality and to problems during continuous preparation of the partly aromatic copolyamides. A particular example of a triamine which can cause such problems is dihexamethylenetriamine, which is formed from the hexamethylenediamine used as a monomer.

The aqueous solutions used have, as a rule, a monomer content of from 30 to 70, in particular from 40 to 65, % by weight.

The aqueous salt solution is passed, advantageously at from 50 to 100°C, continuously into an evaporator zone, where the aqueous salt solution is heated to 250-330°C under superatmospheric pressure of from 1 to 10, preferably from 2 to 6, bar. The temperature used is of course above the melting point of the particular polyamide to be prepared.

As stated above, it is essential that the



residence time in the evaporator zone is not more than 60, preferably from 10 to 55, in particular from 10 to 40, seconds.

5       The conversion on emergence from the evaporator zone is advantageously not less than 93%, preferably from 95 to 98%, and the water content is preferably from 2 to 5, in particular from 1 to 3, % by weight.

10       The evaporator zone is advantageously in the form of a tube bundle. Tube bundles in which the cross-section of the individual tubes is alternately tubular and slot-like have proven particularly useful.

15       As a rule, a residence time of from 1 to 15 minutes is maintained in the mass transfer zone. The mass transfer zone is advantageously in the form of a tube bundle.

20       The two-phase vapor/prepolymer mixture emerging from the evaporator or mass transfer zone is separated. Separation is effected as a rule automatically on the basis of the physical differences in a vessel, the lower part of the vessel advantageously being in the form of a polymerization zone. The vapors liberated essentially consist of steam and diamines, which were liberated on evaporation of the water. These vapors are passed into a column and rectified. Examples of suitable columns are  
25       packed columns, bubble tray columns or sieve tray columns having from 5 to 15 theoretical plates. The column is advantageously operated under pressure conditions identical to those in the evaporator zone. The diamines present in the vapors are separated off and recycled to  
30       the evaporator zone. It is also possible to feed the diamines to the downstream polymerization zone. The rectified steam obtained is taken off at the top of the column.

35       The resulting prepolymer, which, depending on its conversion, essentially consists of low molecular weight polyamide and may contain residual amounts of unconverted salts and as a rule has a relative viscosity of from 1.2

to 1.7, is passed into a polymerization zone. In the polymerization zone, the melt obtained is subjected to polycondensation at from 250 to 330°C, in particular from 270 to 310°C, and under superatmospheric pressure of from 1 to 10, in particular 2 to 6, bar. Advantageously, the vapors liberated here are rectified together with the abovementioned vapors in the column, a residence time of from 5 to 30 minutes advantageously being maintained in the polycondensation zone. The polyamide thus obtained, which as a rule has a relative viscosity of from 1.2 to 2.3, is removed continuously from the condensation zone.

In a preferred procedure, the polyamide thus obtained is passed in molten form through a discharge zone with simultaneous removal of the residual water present in the melt. Examples of suitable discharge zones are devolatilization extruders. The melt freed from water in this manner is then extruded and the extrudates are granulated. The granules obtained are advantageously subjected to solid-phase condensation by means of superheated steam at below the melting point, for example from 170 to 240°C, until the desired viscosity is obtained. The steam obtained at the top of the column is advantageously used for this purpose.

The relative viscosity, measured in 1% strength solution (1 g/100 ml) in 96% strength by weight  $H_2SO_4$  at 23°C, is in general from 2.2 to 5.0, preferably from 2.3 to 4.5, after the solid-phase postcondensation.

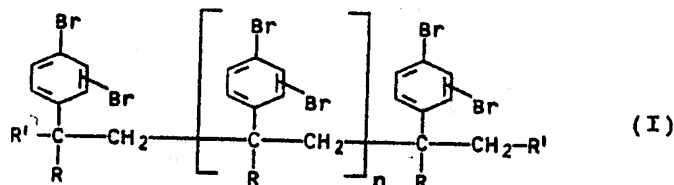
In another preferred procedure, the polyamide melt discharged from the polycondensation zone is passed into a further polycondensation zone, where it is subjected to condensation with continuous formation of new surfaces at from 285 to 310°C, advantageously under reduced pressure, for example from 1 to 500 mbar, until the desired viscosity is obtained. Suitable apparatuses are known as finishers.

Another process which is similar to the one described above is described in EP-A 129 196, to which

reference may be made for further details of the process.

The novel molding materials contain, as component B), 1-30, preferably 1-25, in particular 1-20, % by weight of a brominated polystyrene or of a brominated styrene oligomer or of a mixture thereof.

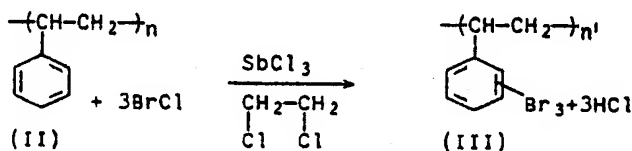
The brominated oligostyrenes used as flameproofing agents have a mean degree of polymerization (number average) of from 3 to 90, preferably from 5 to 60, measured by vapor pressure osmometry in toluene. Cyclic oligomers are also suitable. In a preferred embodiment of the invention, the brominated oligomeric styrenes to be used are of formula I below, where R is hydrogen or an aliphatic radical, in particular alkyl, eg. CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, and n is the number of repeating building blocks in the chain. R' may be H, bromine or a fragment of a conventional free radical initiator:



n may be 1-88, preferably 3-58. The brominated oligostyrenes contain from 40 to 80, preferably from 55 to 70, % by weight of bromine. A product which predominantly consists of polydibromostyrene is preferred. The substances can be melted without decomposition and are soluble in, for example, tetrahydrofuran. They can be prepared either by bromination of the nucleus of styrene oligomers which may be aliphatically hydrogenated, as obtained, for example, by thermal polymerization of styrene (according to German Laid-Open Application DOS 2,537,385) or by free radical oligomerization of suitable brominated styrenes. The flameproofing agent can also be prepared by ionic oligomerization of styrene and subsequent bromination. The amount of brominated oligostyrene required for flameproofing the polyamides depends on the

bromine content. The bromine content of the novel molding materials is from 4 to 20, preferably from 5 to 12, % by weight.

5 The brominated polystyrenes according to the invention are usually obtained by the process described in EP-A 47 549:



10 The brominated polystyrenes obtainable by this process and commercially available are predominantly tribrominated products substituted in the nucleus.  $n'$  (cf. III) is generally from 125 to 1,500, corresponding to a molecular weight of from 42,500 to 235,000, preferably from 130,000 to 235,000.

15 The bromine content (based on the content of bromine substituted in the nucleus) is in general not less than 55, preferably not less than 60, in particular 65, % by weight.

The commercial powder products generally have a glass transition temperature of from 160 to 200°C.

20 It is also possible to use mixtures of the brominated oligostyrenes with brominated polystyrenes in the novel molding materials, any mixing ratio being possible.

25 The novel molding materials contain, as component C), 1-15, preferably 1-10, in particular 2-5, % by weight of a synergistic metal oxide or metal borate or a mixture thereof. In general, zinc oxide, lead oxide, iron oxide, alumina, tin oxide and magnesium oxide or mixtures thereof are suitable as synergistic metal oxides. Antimony trioxide and/or antimony pentoxide are preferred.

30 Suitable metal borates are borates of metals of main groups 1 to 3 and of subgroups 1 to 8 of the Periodic Table, anhydrous zinc borate or zinc borate of

the general formula (IV)



5 where x is from 3.3 to 3.7 being preferred. This zinc borate is essentially stable at high processing temperatures of the partly aromatic polyamides and does not tend to eliminate the water of hydration to any significant extent. Accordingly, zinc borates having a high content of water of hydration are generally not so suitable as synergistic agents.

10 It is also possible to use mixtures of metal borates with metal oxides, any mixing ratio being possible.

Mixtures of antimony trioxide with anhydrous zinc borate are preferred.

15 The novel molding materials may contain, as component D), not more than 60, preferably from 5 to 50, % by weight of fibrous or particulate fillers or of a mixture thereof. Examples of fillers are asbestos, carbon fibers or glass fibers in the form of woven glass fabrics, glass mats or glass rovings, glass spheres and wollastonite.

20 Preferred fibrous reinforcing substances (component D) are carbon fibers, potassium titanate whiskers, Aramid fibers and particularly preferably glass fibers. When glass fibers are used, they may be treated with a size and an adhesion promoter for better compatibility with the thermoplastic polyamide (A). In general, the glass fibers used have a diameter of from 6 to 20  $\mu\text{m}$ .

25 These glass fibers may be incorporated both in the form of short glass fibers and in the form of rovings. In the finished injection molding, the mean length of the glass fibers is preferably from 0.08 to 0.5 mm.

30 Suitable particulate fillers are amorphous silica, asbestos, magnesium carbonate (chalk), powdered quartz, mica, talc, feldspar and in particular calcium silicates, such as wollastonite and kaolin (in particular calcined kaolin).

Surprisingly, the novel molding materials have, as desired, classification V-O according to UL 94, even with high contents of particulate fillers.

5 Preferred combinations of fillers are, for example, 20% by weight of glass fibers with 15% by weight of wollastonite and 15% by weight of glass fibers with 15% by weight of wollastonite.

10 As a further component E), a rubber impact modifier (elastomer) may be present in the novel thermoplastic molding materials, in amounts of not more than 20, preferably from 1 to 10, % by weight.

Elastomers based on ethylene, propylene, butadiene or acrylates or mixtures of these monomers may be mentioned merely as examples of rubber impact modifiers.

15 Polymers of this type are described in, for example, Houben-Weyl, Methoden der organischen Chemie, Vol. 14/1 (Georg-Thieme-Verlag, Stuttgart, 1961), pages 392-406, and in the monograph by C.B. Bucknall, Toughened Plastics (Applied Science Publishers, London, 1977).

20 Some preferred types of such elastomers are described below.

A first preferred group comprises the ethylene/propylene (EP) and ethylene/propylene/diene (EPDM) rubbers, which preferably have a ratio of ethylene radicals to propylene radicals of from 40 : 60 to 65 : 35.

25 The Mooney viscosities (MLI+4/100°C) of such non-crosslinked EP and EPDM rubbers (gel contents generally less than 1% by weight) are preferably from 25 to 100, in particular from 35 to 90 (measured using the large rotor after a running time of 4 minutes at 100°C according to DIN 53,523).

30 EP rubbers generally have virtually no double bonds, whereas EPDM rubbers may have from 1 to 20 double bonds per 100 carbon atoms.

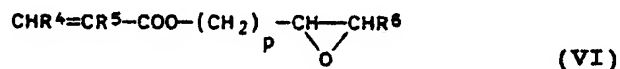
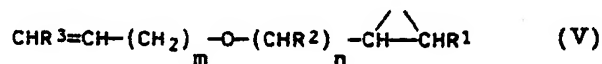
35 Examples of diene monomers for EPDM rubbers are conjugated dienes, such as isoprene and butadiene, nonconjugated dienes of 5 to 25 carbon atoms, such as

1,4-butadiene, 1,4-hexadiene, 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene and 1,4-octadiene, cyclic dienes, such as cyclopentadiene, cyclohexadiene, cyclooctadiene and dicyclopentadiene, and alkenyl norbornenes, such as 5-ethylidene-2-norbornene, 5-butylidene-2-norbornene, 2-methyl-5-norbornene and 2-isopropenyl-5-norbornene, and tricyclobutenes, such as 3-methyltricyclo-[5.2.1.0.2.6]-3,8-decadiene, or mixtures thereof. 1,5-Hexadiene, 5-ethylidenenorbornene and dicyclopentadiene are preferred. The diene content of EPDM rubbers is preferably from 0.5 to 10, in particular from 1 to 8, % by weight, based on the total weight of the rubber.

EP and EPDM rubbers can also be grafted with reactive carboxylic acids or their derivatives. Acrylic acid, methacrylic acid and their derivatives and maleic anhydride may be mentioned here merely as typical examples.

Another group of preferred rubbers comprises copolymers of ethylene with acrylates and/or methacrylates, in particular those which additionally contain epoxy groups. These epoxy groups are preferably incorporated in the rubber by adding to the monomer mixture the epoxy-containing monomers of the general formula V or VI

25



30

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  are each hydrogen or alkyl of 1 to 6 carbon atoms,  $m$  is an integer of from 0 to 20,  $n$  is an integer of from 0 to 10 and  $p$  is an integer of from 0 to 5.

Preferably,  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are each hydrogen,  $m$  is 0 or 1 and  $n$  is 1. The corresponding compounds are alkyl

glycidyl ethers or vinyl glycidyl ethers.

5 Preferred examples of compounds of the formula (VI) are epoxy-containing esters of acrylic acid and/or methacrylic acid, of which glycidyl acrylate and glycidyl methacrylate are particularly preferred.

The ethylene content of the copolymers is in general from 50 to 98% by weight, and the amount of epoxy-containing monomers and the amount of acrylate and/or methacrylate are each from 1 to 49% by weight.

10 Particularly preferred copolymers are those consisting of  
from 50 to 98.9, in particular from 60 to 95, % by weight of ethylene,  
15 from 0.1 to 40, in particular from 2 to 20, % by weight of glycidyl acrylate, glycidyl methacrylate, acrylic acid and/or maleic anhydride, and  
from 1 to 45, in particular from 10 to 35, % by weight of n-butyl acrylate and/or 2-ethylhexyl acrylate.

20 Other preferred esters of acrylic and/or methacrylic acid are the methyl, ethyl, propyl, isobutyl and tert-butyl esters.

Vinyl esters and vinyl ethers may also be used as comonomers.

25 The ethylene copolymers described above can be prepared by conventional processes, preferably by random copolymerization under superatmospheric pressure at elevated temperatures. Corresponding processes are described in the literature.

30 The melt flow index of the ethylene copolymers is in general from 1 to 80 g/10 min (measured at 190°C and under a load of 2.16 kg).

35 Other preferred elastomers (rubbers) E) are graft copolymers with butadiene, butadiene/styrene, butadiene/acrylonitrile and acrylates, as described in, for example, DE-A-16 94 173 and DE-A-23 48 377.

Particular examples of these are the ABS polymers, as described in DE-A-20 35 390, DE-A-22 48 242



and EP-A-22 216, those stated in EP-A-22 216 being particularly preferred.

Other suitable rubbers E) are graft polymers of from 25 to 98% by weight of an acrylate rubber having a glass transition temperature of less than  $-20^{\circ}\text{C}$ , as the grafting base,

and

from 2 to 75% by weight of a copolymerizable ethylenically unsaturated monomer whose homopolymers and copolymers have a glass transition temperature of more than  $25^{\circ}\text{C}$ , as the graft.

The grafting bases are acrylate or methacrylate rubbers, and up to 40% by weight of further comonomers may be present. The  $\text{C}_1\text{-C}_8$ -esters of acrylic acid or methacrylic acid and their halogenated derivatives, as well as aromatic acrylates and mixtures thereof, are preferred. Acrylonitrile, methacrylonitrile, styrene,  $\alpha$ -methylstyrene, acrylamides, methacrylamides and vinyl- $\text{C}_1\text{-C}_6$ -alkyl ethers may be mentioned as comonomers in the grafting base.

The grafting base may be noncrosslinked or partially or completely crosslinked. Crosslinking is achieved by copolymerization of, preferably, from 0.02 to 5, in particular from 0.05 to 2, % by weight of a crosslinking monomer having more than one double bond. Suitable crosslinking monomers are described in, for example, DE-A-27 26 256 and EP-A-50 265.

Preferred crosslinking monomers are triallyl cyanurate, triallyl isocyanurate, triacryloylhexahydro-s-triazine and trialkylbenzenes.

If the crosslinking monomers have more than 2 polymerizable double bonds, it is advantageous to restrict their amount to not more than 1% by weight, based on the grafting base.

Particularly preferred grafting bases are emulsion polymers having a gel content of more than 60% by weight (determined in dimethylformamide at  $25^{\circ}\text{C}$  according

to M. Hoffmann, H. Krömer and R. Kuhn, Polymeranalytik, Georg-Thieme-Verlag, Stuttgart, 1977).

Other suitable grafting bases are acrylate rubbers having a diene core, as described in, for example, EP-A-50 262.

Particularly suitable graft monomers are styrene,  $\alpha$ -methylstyrene, acrylonitrile, methacrylonitrile and methyl methacrylate and mixtures thereof, in particular those of styrene and acrylonitrile in a weight ratio of from 90 : 10 to 50 : 50.

The grafting yield, ie. the quotient of the amount of grafted monomer to the amount of graft monomer used is in general from 20 to 80%.

Rubbers based on acrylates, which may be used according to the invention, are described in, for example, DE-A-24 44 584 and DE-A-27 26 256.

The rubbers E) preferably have a glass transition temperature of less than  $-30^{\circ}\text{C}$ , in particular less than  $-40^{\circ}\text{C}$ , which leads to good impact strength even at low temperatures.

It is of course also possible to use mixtures of the abovementioned elastomers which impart impact strength.

In addition to components A) to E), the novel molding materials may contain conventional additives and processing assistants. The amount of these is in general not more than 20, preferably not more than 10, % by weight, based on the total weight of components A) to E).

Examples of conventional additives are stabilizers and antioxidants, heat stabilizers and UV stabilizers, lubricants and mold release agents, colorants, such as dyes and pigments, nucleating agents and plasticizers.

Antioxidants and heat stabilizers which may be added to the thermoplastic materials according to the invention are, for example, halides of metals of Group I of the Periodic Table, for example sodium halides,

potassium halides and lithium halides, if necessary in combination with copper(I) halides, eg. chlorides, bromides or iodides. Sterically hindered phenols, hydroquinones, substituted members of this group and mixtures thereof may also be used, preferably in concentrations of not more than 1% by weight, based on the weight of the molding material.

Examples of UV stabilizers are various substituted resorcinols, salicylates, benzotriazoles and benzophenones, which are used in general in amounts of not more than 2.0% by weight.

Lubricants and mold release agents, which are added as a rule in amounts of not more than 1% by weight to the thermoplastic material, are stearic acid, stearates, stearyl alcohol, alkyl stearates and stearamides, as well as esters of pentaerythritol with long-chain fatty acids.

The additives include stabilizers which prevent dehydrobromination of component B), so that the processing stability is increased and the corrosion effect decreased. Such stabilizers are, for example, salts of mono- or bifunctional fatty acids, such as calcium behenate, calcium stearate, barium stearate and lead phthalate, calcium carbonate, organic tin compounds, such as cyclic dibutyltin sulfide or butylthiostannous acid and hydrogen phosphates, eg.  $\text{Na}_2\text{HPO}_4$ .

The novel molding materials can be prepared by conventional processes, by mixing the starting components in a conventional mixing apparatus, such as an extruder, a Brabender mill or a Banbury mill, and then extruding the mixture. After extrusion, the extrudate is cooled and comminuted. The mixing temperatures are in general from 280 to 350°C.

It is in principle also possible, and sometimes advantageous, first to mix the low molecular weight component A) with B) and C) and, if necessary, D) and E) and then to carry out solid-phase postcondensation.

It may also be advantageous to incorporate the synergistic agents in the form of a masterbatch of polyamide or polyethylene.

5 The novel molding materials have a good overall spectrum of mechanical properties. The moldings have a pale intrinsic color and are toxicologically acceptable in use. In addition to the good flame resistance, they have good electrical properties, in particular good creep resistance and dielectric strength. Because of the  
10 extremely good stability to various soldering processes, the novel molding materials are particularly suitable for the production of injection molded circuit boards, which may also contain integrated functional elements and may be readily copper-plated.

15 The novel molding materials are also suitable for the production of, in particular, compact housings and other components for electronic equipment, high requirements being set for the heat distortion resistance.

#### EXAMPLES

20 The following components were used:  
Component A)

The preparation was carried out according to EP 129 195.

25 An aqueous solution, consisting of 35 kg of  $\epsilon$ -caprolactam, 55 kg of terephthalic acid and 38.5 kg of hexamethylenediamine and 128.5 kg of water, was conveyed from a heated storage container at about 80°C at a rate corresponding to an amount of polyamide of 5 kg/hour, by means of a metering pump, into a tubular evaporator  
30 arranged partly horizontally and partly vertically. The evaporator was heated by means of a liquid heating medium, which was at 295°C, with vigorous circulation. The evaporator had a length of 3 m, a capacity of 180 ml and a heat-transfer surface area of about 1300 cm<sup>2</sup>. The  
35 residence time in the evaporator was 50 seconds. The prepolymer/steam mixture emerging from the evaporator was at 290°C and was separated into steam and melt in a

separator. The melt remained in the separator for a further 10 minutes and was then extruded by means of an extruder having a devolatilization zone, and the extrudate was solidified in a water bath and then granulated.

5 The separator and the evaporator zone were kept under a pressure of 5 bar by a pressure regulating means arranged downstream of the column. The steam separated off in the separator was fed to a packed column which had about 10 theoretical plates and into which about 1 l of vapor

10 condensate per hour was introduced at the top to generate a reflux. The resulting temperature at the top of the column was 152°C. The steam emerging downstream of the let-down valve was condensed, and it contained less than 0.05% by weight of hexamethylenediamine and less than

15 0.1% by weight of  $\epsilon$ -caprolactam. An aqueous solution of hexamethylenediamine, which contained 80% by weight of hexamethylenediamine and from 1 to 3% of  $\epsilon$ -caprolactam, based in each case on polyamide produced, was obtained as a bottom product of the column. This solution was added

20 to the starting salt solution again by means of a pump before the starting salt solution entered the evaporator.

Downstream of the evaporator, the prepolymer had a relative viscosity of 1.25, measured in 96% strength by weight sulfuric acid at 20°C and, according to terminal

25 group analysis, had a conversion of from 93 to 95%. The content of bishexamethylenetriamine was from 0.1 to 0.15% by weight, based on polyamide.

After emergence of the polymer melt from the separator, the polyamide had a very pale intrinsic color

30 and an extremely low content of bishexamethylenetriamine of 0.17% and a relative viscosity of from 1.65 to 1.80.

The product had roughly equivalent amounts of terminal carboxyl and amino groups.

The content of extractables (extraction with

35 methanol) was from 3.1 to 3.3% by weight.

In the extruder, the melt was then let down to atmospheric pressure and underwent virtually no further

condensation during a residence time of less than 1 minute. The resulting granules were subjected to continuous solid-phase condensation using superheated steam at 195°C during a residence time of 30 hours until a final viscosity  $\eta$  rel of 2.50 was obtained. The content of extractables was then 0.2% by weight (methanol extract).  
Component B)

Brominated polystyrene having a bromine content (content of bromine substituted in the nucleus) of 67% (Pyro-check® 68 PB from Ferro Corporation)  
Component C)

Antimony trioxide having a density of from 5.2 to 5.8 g/cm<sup>3</sup>  
Component D1)

Glass fibers having a mean diameter of 10  $\mu$ m.  
Component D2)

Wollastonite having a median particle size ( $d_{50}$ ) of 10  $\mu$ m and a specific surface area of 5 m<sup>2</sup>/g.  
Component E)

An olefin copolymer of  
59.8% by weight of ethylene,  
35% by weight of n-butyl acrylate,  
4.5% by weight of acrylic acid and  
0.7% by weight of maleic anhydride,  
having a melt flow index MFI of 10 g/10 min at 190°C and under a load of 2.16 kg.

This copolymer was prepared by copolymerization of the monomers at elevated temperatures and under super-atmospheric pressure.

The components were mixed in a twin-screw extruder at 300-350°C, and the mixture was extruded into a water bath. Component E) was added to the melt first. After granulation and drying, the test specimens were produced on an injection molding machine and were tested.

The fire test was carried out according to UL 94 using 1/8, 1/16 and 1/32 inch test specimens with conventional conditioning. The LOI (lowest oxygen index) was

determined according to ASTM D 2863-77.

The creep resistance was determined according to IEC 112/1979, the modulus of elasticity according to DIN 53,457 and the impact strength according to DIN 53,453.

5

The composition of the molding materials and the results of the measurements are shown in the Table.

TABLE

No.	Composition [% by weight]	Fire behavior according to UL 94 1/8' 1/16' 1/32'	LOI	Creep resistance [volt]	Modulus of elasticity [N/mm <sup>2</sup> ]
1	54.9 A 16.3 B 3.8 C 25 D1 -	V-O V-O V-O	28.7	500/400*	9800
2	52.1 A 15 B 2.9 C 15 D1+ - 15 D2	V-O V-O V-O	30.2	450/425*	8300
3	48 A 15 B 3 C 30 D2 4 E	V-O V-O V-O	28.5	450/375*	5300
4	47.3 A 15 B 3.7 C 15 D1+ 4 E 15 D2	V-O V-O V-O	28.5	475/400*	8200
5	44.6 A 14.8 B 2.6 C 15 D1+ 8 E 15 D2	V-O V-O V-O	27.0	-	7500

\*) CTI/CTI (M)

Impact strength  
23°C [kJ/m<sup>2</sup>]

1	30
2	26
3	40
4	32
5	33



We claim:-

1. A flameproofed, thermoplastic molding material containing, as essential components,
  - A) 10-98% by weight of a partly aromatic copolyamide, essentially composed of
    - a<sub>1</sub>) from 40 to 90% by weight of units derived from terephthalic acid and hexamethylenediamine,
    - a<sub>2</sub>) from 0 to 50% by weight of units derived from  $\epsilon$ -caprolactam and
    - a<sub>3</sub>) from 0 to 60% by weight of units derived from adipic acid and hexamethylenediamine,components a<sub>2</sub>) and/or a<sub>3</sub>) accounting in total for not less than 10% by weight of the total number of units,
  - B) 1-30% by weight of a brominated polystyrene or a brominated styrene oligomer or of a mixture thereof,
  - C) 1-15% by weight of a synergistic metal oxide or metal borate or a mixture thereof and in addition
  - D) 0-60% by weight of a fibrous or particulate filler or a mixture thereof and
  - E) 0-20% by weight of an elastomeric polymer.
2. A flameproofed thermoplastic molding material as claimed in claim 1, containing
  - 35-97% by weight of A),
  - 1-20% by weight of B),
  - 1-10% by weight of C) and
  - 1-35% by weight of D).
3. A flameproofed thermoplastic molding material as claimed in claim 1, containing
  - 25-87% by weight of A),
  - 1-20% by weight of B),
  - 1-10% by weight of C),
  - 10-35% by weight of D) and
  - 1-10% by weight of E).

4. A flameproofed thermoplastic molding material as claimed in claim 1, wherein the partly aromatic copolyamides A) have a triamine content of less than 0.5% by weight.

5. A flameproofed thermoplastic molding material as claimed in claim 1, wherein the component A) is composed of

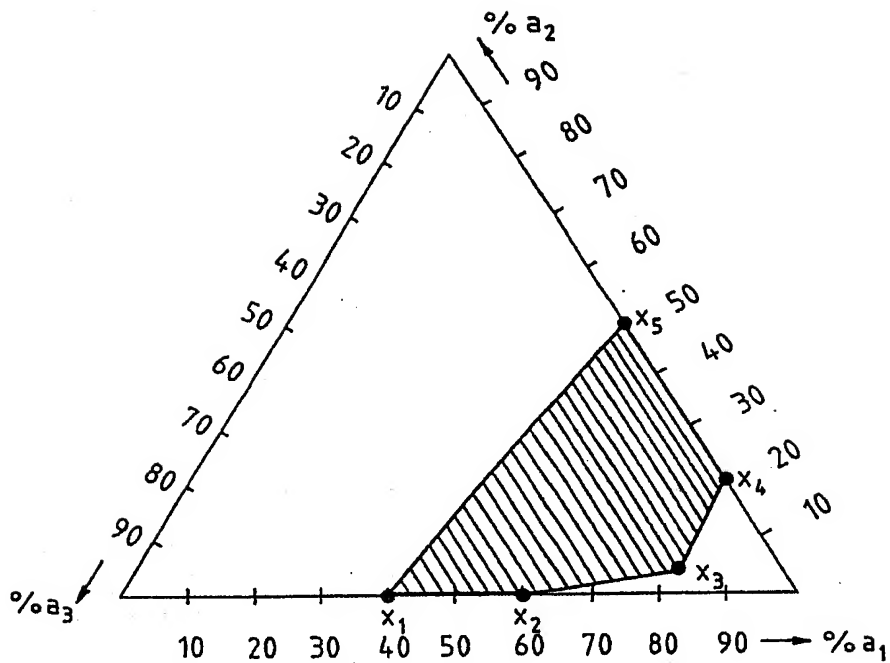
- a<sub>1</sub>) from 50 to 80% by weight of units derived from terephthalic acid and hexamethylenediamine and
- a<sub>2</sub>) from 20 to 50% by weight of units derived from ε-caprolactam.

6. A flameproofed thermoplastic molding material as claimed in claim 1, wherein the brominated polystyrene (component B) has a bromine content of not less than 55% by weight.

7. A flameproofed thermoplastic molding material as claimed in claim 1, wherein the brominated styrene oligomer (component B) has a bromine content of not less than 40% by weight.

8. A flameproofed thermoplastic molding material as claimed in claim 1, wherein the component C) consists of antimony trioxide or zinc oxide or lead oxide or iron oxide or zinc borate or a mixture thereof.

9. A molding obtainable from a thermoplastic molding material as claimed in claim 1.



*Robt*

Patent Agents.

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